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indices can be estimated by assuming the atomic arrangements within the crystal unit cell and neglecting the uncertain effects of the internal field. Furthermore, the form birefringence cannot be neglected because a number of voids were observed within the drawn specimens under scanning electron microscopy.[27] Unfortunately, there is no way at present to estimate the form birefringence in our laboratory. The result in Figure 11 indicates that as a crude approximation, the temperature dependence of the molecular orientation cannot be observed from birefringence data in spite of a significant transition from crystalline to amorphous as shown in Figure 7. This means that birefringence is not sensitive enough to detect small changes in the molecular orientation due to the transition because of the small difference in the values of Δ_c° (58.5×10^{-3}) and Δ_a° (52×10^{-3}). Accordingly, an experimental method for this purpose is needed. It is evident that since the crystal lattice modulus is independent of temperature, the temperature dependence of the Young's modulus is due to an increase in amorphous content and a decrease in the amorphous modulus with increasing temperature.

Conclusion

The temperature dependence of the crystal lattice modulus was measured by X-ray diffraction with use of ultradrawn films with elongation ratios >300. The modulus is in the range 211-222 GPa and is independent of temperature up to 145 °C, which is close to the equilibrium melting point. This behavior is quite different from that of bulk specimens. Measurement of the complex dynamic tensile modulus indicates that the storage modulus E' decreases with increasing temperature, even for ultradrawn films ($\lambda = 400$) whose E' at 20 °C is 216 GPa. The thermal expansion coefficient of the crystal c axis was -2.27×10^{-5}/°C. In contrast, the thermal expansion coefficient of bulk polymer in the stretching direction was positive.

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Mathematical Treatment of the Temperature Dependence of the Crystal Lattice Modulus and the Young's Modulus of Polyethylene

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ABSTRACT: A mathematical representation based on linear elastic theory is proposed for investigating the temperature dependence of the crystal lattice modulus in the chain direction and the Young's modulus. Mathematical formulation was carried out for a composite model of crystalline and amorphous phases. This description indicates that the crystal lattice modulus and the linear thermal coefficient as measured by X-ray diffraction are different from the intrinsic crystal lattice modulus and the coefficient. The calculated results are in good agreement with the experimental results for an ultradrawn polyethylene film with a draw ratio of 400, showing that the crystal lattice modulus is independent of temperature while the Young's modulus decreases with increasing temperatures.

Introduction

In the preceding article,[1] the temperature dependence of the crystal lattice modulus was measured by X-ray diffraction with use of ultradrawn films with elongation ratios in excess of 300. The modulus is in the range 211-222 GPa and is independent of temperature up to 145 °C, which is close to the equilibrium point. In contrast, measurement of the complex dynamic tensile modulus indicated that the storage modulus E' decreases with increasing temperature, even for an ultradrawn film ($\lambda = 400$) whose E' at 20 °C is 216 GPa. This discrepancy was related to an increase in the amorphous content with increasing temperature. Furthermore, the thermal expansion coefficient of the crystal c axis was -2.27×10^{-5}/°C, while the thermal expansion coefficient of bulk polymer in the stretching direction was positive. This contradictory be-

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$$|a| = \begin{vmatrix} \cos\phi\cos\theta\cos\eta - \sin\phi\sin\eta & -\cos\phi\cos\theta\sin\eta - \sin\phi\sin\eta & \cos\phi\sin\theta \\ \sin\phi\cos\theta\cos\eta + \cos\phi\sin\eta & -\sin\phi\cos\theta\sin\eta + \cos\phi\cos\eta & \sin\phi\sin\theta \\ -\sin\theta\cos\eta & \sin\theta\sin\eta & \cos\theta \end{vmatrix} \quad (2)$$

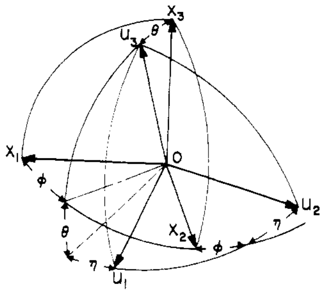

Figure 1. Eulerian angles θ, ϕ, and η, which specify the orientation of Cartesian coordinates $0\text{–}u_1u_2u_3$ fixed in a structural unit, with respect to other coordinates $0\text{–}x_1x_2x_3$ fixed in the bulk specimen.

havior suggests that the thermal expansion coefficient of amorphous chain segments must be positive.

The present article investigates the above phenomenon theoretically. A mathematical representation of the crystal lattice modulus along the molecular chain axis is discussed in terms of the geometrical arrangement of the bulk specimen as revealed by X-ray analysis. For convenience in mathematical representation, a composite unit is proposed as a model system, in which anisotropic amorphous layers lie adjacent to oriented composite layers with the interface perpendicular to the stretching direction.[2] The crystal lattice modulus is calculated as functions of temperature, crystallinity, and molecular orientation. The calculated results are discussed in relation to the experimental observation in the preceding article.[1]

Mathematical Representation of the Temperature Dependence of the Crystal Lattice Modulus and the Young's Modulus in a Semicrystalline Polymer Having an Orthorhombic Unit Cell

A mathematical representation is proposed to estimate the temperature dependence of the crystal lattice modulus as well as the Young's modulus, quantitatively. The procedure for calculating the mechanical anisotropy of a single-phase system from the orientation of the structural units and the intrinsic mechanical anisotropy of the structural unit is first discussed in relation to mutual conversion of the orientation distribution function of the structural unit with respect to Cartesian coordinates fixed within the bulk specimen. Thus Figure 1 shows the Cartesian coordinate $0\text{–}u_1u_2u_3$, fixed in a structural unit, with respect to another Cartesian coordinate $0\text{–}x_1x_2x_3$ fixed in the bulk specimen.

Assuming the homogeneous stress hypothesis for a polycrystalline material, the relation between the intrinsic compliance of the structural unit and the bulk compliance is given by

$$S_{ijkl} = \sum_i\sum_j\sum_k\sum_l \langle a_{io}a_{jp}a_{kq}a_{lr}\rangle S^\circ{}_{opqr} \quad (1)$$

where S_{ijkl} and $S^\circ{}_{opqr}$ are the compliance of the bulk specimen and of the structural unit, respectively. The parameter a_{io} is the direction cosine of the u_o axis with respect to the x_i axis, which is given from the geometrical arrangement in Figure 1 as eq 2. Average values in eq 1, $\langle a_{io}a_{jp}a_{kq}a_{lr}\rangle$, are given by

$$\langle a_{io}a_{jp}a_{kq}a_{lr}\rangle = \int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi} \omega(\theta,\phi,\eta)a_{io}a_{jp}a_{kq}a_{lr}\sin\theta\, d\theta\, d\phi\, d\eta \quad (3)$$

where $\omega(\theta,\phi,\eta)$ is the orientation distribution of the structural unit $0\text{–}u_1u_2u_3$ with respect to the coordinate $0\text{–}x_1x_2x_3$ in Figure 1.

In accordance with Krigbaum and Roe's analysis,[3] this distribution function $\omega(\theta,\phi,\eta)$ may be expanded in a series of spherical harmonics. With some changes from their notation, the generalized orientation factor can be written by using $\omega(\theta,\phi,\eta)$ as follows:

$$F_{lmn} = \int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi} \omega(\theta,\phi,\eta)\, P_{lmn}(\cos\theta)\cos m\phi\cos n\eta \times \sin\theta\, d\theta\, d\phi\, d\eta \quad (4)$$

where

$$P_{lmn}(\cos\theta) = \left\{\frac{1-\cos\theta}{2}\right\}^{(m-n)/2}\left\{\frac{1+\cos\theta}{2}\right\}^{(m+n)/2} P_{l-m}^{(m-n,m+n)}(\cos\theta) \quad (5)$$

and $P_{l-m}^{(m-n,m+n)}(\cos\theta)$ is the Jacobi polynomial defined by

$$P_{l-m}^{(m-n,m+n)}(\cos\theta) = \frac{(l-n)!}{(l-m)!(m-n)!} \times {}_2F_1\{m-l,\, l+m+1;\, m-n+1;\, (1-\cos\theta)/2\} \quad (6)$$

where ${}_2F_1\{m-l,\, l+m+1;\, m-n+1;\, (1-\cos\theta)/2\}$ is the hypergeometric function.

The elastic compliance S_{ijkl}, represented as a tensor quantity, may be related to S_{uv} by a matrix as follows:

$$S_{ijkl} = S_{uv} \qquad u \text{ and } v \le 3$$

$$S_{ijkl} = \tfrac{1}{2}S_{uv} \qquad u \text{ or } v \ge 3$$

$$S_{ijkl} = \tfrac{1}{4}S_{uv} \qquad u \text{ and } v > 3 \quad (7)$$

where (ij) and (kl) become u and v, respectively. The combination is given by

$$(1\,1) \rightarrow 1 \qquad (2\,2) \rightarrow 2 \qquad (3\,3) \rightarrow 3$$

$$(2\,3) \rightarrow 4 \qquad (3\,1) \rightarrow 5 \qquad (1\,2) \rightarrow 6$$

By use of eq 2–7, the elastic compliance $\mathbf{S}_{uv}$ can be formulated as a function of the orientation factors up to the fourth order. These results are shown in the Appendix.

The composite structural unit is represented by the model in Figures 2 and 3.[2] The mechanical anisotropy of a two-phase system is based on the homogeneous stress hypothesis assuming that the structural unit is composed of crystalline and amorphous phases. When the tensile stress σ_{33} at an arbitrary temperature T is applied along the x_3 axis, the inner stresses (σ_{11}^{c}, σ_{22}^{c}, σ_{33}^{c}, 0, 0, 0) and (σ_{11}^{a}, σ_{22}^{a}, σ_{33}^{a}, 0, 0, 0) are applied to the crystalline and amorphous phases, respectively, to induce the following strains in the respective phases:

$$\epsilon_{11}^{\mathrm{c}} = S_{11}^{\mathrm{cv}}\sigma_{11}^{\mathrm{c}} + S_{12}^{\mathrm{cv}}\sigma_{22}^{\mathrm{c}} + S_{13}^{\mathrm{cv}}\sigma_{33}^{\mathrm{c}} + \alpha_{11}^{\mathrm{cv}}\Delta T$$

$$\epsilon_{22}^{\mathrm{c}} = S_{12}^{\mathrm{cv}}\sigma_{11}^{\mathrm{c}} + S_{11}^{\mathrm{cv}}\sigma_{22}^{\mathrm{c}} + S_{13}^{\mathrm{cv}}\sigma_{33}^{\mathrm{c}} + \alpha_{22}^{\mathrm{cv}}\Delta T$$

$$\epsilon_{33}^{\mathrm{c}} = S_{13}^{\mathrm{cv}}\sigma_{11}^{\mathrm{c}} + S_{13}^{\mathrm{cv}}\sigma_{22}^{\mathrm{c}} + S_{33}^{\mathrm{cv}}\sigma_{33}^{\mathrm{c}} + \alpha_{33}^{\mathrm{cv}}\Delta T$$

$$\epsilon_{12}^{\mathrm{c}} = \epsilon_{23}^{\mathrm{c}} = \epsilon_{31}^{\mathrm{c}} = 0 \quad (8)$$

$$\epsilon_{11}^{\mathrm{a}} = S_{11}^{\mathrm{av}}\sigma_{11}^{\mathrm{a}} + S_{12}^{\mathrm{av}}\sigma_{22}^{\mathrm{a}} + S_{13}^{\mathrm{av}}\sigma_{33}^{\mathrm{a}} + \alpha_{11}^{\mathrm{av}}\Delta T$$

$$\epsilon_{22}^{\mathrm{a}} = S_{12}^{\mathrm{av}}\sigma_{11}^{\mathrm{a}} + S_{11}^{\mathrm{av}}\sigma_{22}^{\mathrm{a}} + S_{13}^{\mathrm{av}}\sigma_{33}^{\mathrm{a}} + \alpha_{22}^{\mathrm{av}}\Delta T$$

$$\epsilon_{33}^{\mathrm{a}} = S_{13}^{\mathrm{av}}\sigma_{11}^{\mathrm{a}} + S_{13}^{\mathrm{av}}\sigma_{22}^{\mathrm{a}} + S_{33}^{\mathrm{av}}\sigma_{33}^{\mathrm{a}} + \alpha_{33}^{\mathrm{av}}\Delta T$$

$$\epsilon_{12}^{\mathrm{a}} = \epsilon_{23}^{\mathrm{a}} = \epsilon_{31}^{\mathrm{a}} = 0 \quad (9)$$

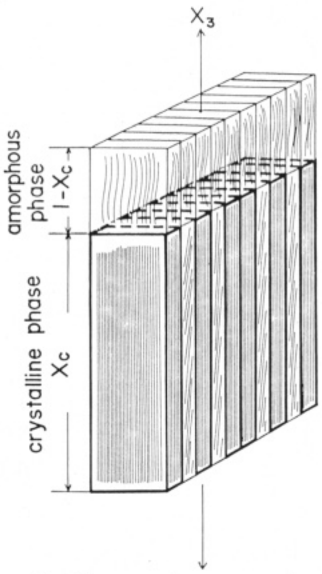

Figure 2. Schematic diagram of a proposed series model with multi-ply layers for an anisotropy of a semicrystalline polymer.

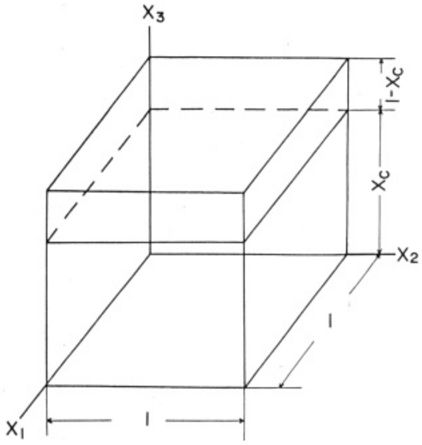

Figure 3. Composite structural unit of a semicrystalline polymer, in which the crystalline and amorphous phases are connected at the face perpendicular to the x_3 axis.

where $S^{\mathrm{cv}}_{\mathrm{uv}}$ and $S^{\mathrm{av}}_{\mathrm{uv}}$ represent the average elastic compliance of the crystalline and amorphous phases, respectively. On the basis of the experimental results in the preceding article,[1] S^{av}_{uv} is given as a function of temperature, while S^{cv}_{uv} is independent of temperature. This treatment is discussed later. Parameters $\alpha^{\mathrm{cv}}_{uu}$ and $\alpha^{\mathrm{av}}_{uu}$ represent the average thermal expansion coefficients of the crystalline and amorphous phases, respectively. ΔT is given by $T - T_0$, where T_0 is the reference temperature.

The crystallinity of ultradrawn polyethylene with a draw ratio of 400 is >97% at room temperature. Although the amorphous phase in such a highly crystalline system at room temperature should be indistinguishable from the crystalline phase, the amorphous phase can be distinguished at elevated temperature, since the amorphous content increases by transition from the crsytalline phase at the crystallite boundaries. Accordingly, the proposed model in Figure 2 does not represent the structure of the bulk specimen at room temperature. However, representing the temperature dependence of the Young's modulus requires a complicated model, and a simple two-phase model is used in this article for the mathematical analysis.

The uniaxial stress condition with respect to the x_3 axis leads to the following relations:[4]

$$\begin{gathered}\sigma_{11} = X_{\mathrm{c}}\sigma^{\mathrm{c}}_{11} + (1 - x_{\mathrm{c}})\sigma^{\mathrm{a}}_{11} = 0\\ \sigma_{22} = X_{\mathrm{c}}\sigma^{\mathrm{c}}_{22} + (1 - X_{\mathrm{c}})\sigma^{\mathrm{a}}_{22} = 0\\ \sigma_{33} = \sigma^{\mathrm{c}}_{33} = \sigma^{\mathrm{a}}_{33}\end{gathered} \tag{10}$$

where σ_{uu} corresponds to the stress of the bulk specimen. For the above restriction upon the strain, one has

$$\begin{gathered}\epsilon_{11} = \epsilon^{\mathrm{c}}_{11} = \epsilon^{\alpha}_{11}\\ \epsilon_{22} = \epsilon^{\mathrm{c}}_{22} = \epsilon^{\mathrm{c}}_{22}\\ \epsilon_{33} = X_{\mathrm{c}}\epsilon^{\mathrm{c}}_{33} + (1 - X_{\mathrm{c}})\epsilon^{\mathrm{a}}_{33}\\ \epsilon_{12} = \epsilon_{23} = \epsilon_{31} = 0\end{gathered} \tag{11}$$

The average linear thermal expansion coefficients $\alpha^{\mathrm{cv}}_{uu}$ and $\alpha^{\mathrm{av}}_{uu}$ in the crystalline and amorphous phases, respectively, in eq 8 and 9 are given by

$$\alpha^{\mathrm{cv}}_{11} = {}^1\!/_{12}(2F_{200} - F_{202} + 4)(\alpha^{\mathrm{co}}_{11} + \alpha^{\mathrm{co}}_{22}) + {}^1\!/_3(1 - F_{200})\alpha^{\mathrm{co}}_{33} \tag{12}$$

$$\alpha^{\mathrm{cv}}_{33} = {}^1\!/_3(1 - F_{200})(\alpha^{\mathrm{co}}_{11} + \alpha^{\mathrm{co}}_{22}) + {}^1\!/_3(2F_{200} + 1)\alpha^{\mathrm{co}}_{33} \tag{13}$$

$$\alpha^{\mathrm{av}}_{11} = {}^1\!/_6(F^{\mathrm{am}}_{200} + 2)(\alpha^{\mathrm{ao}}_{11} + \alpha^{\mathrm{ao}}_{22}) + {}^1\!/_3(1 - F^{\mathrm{am}}_{200})\alpha^{\mathrm{ao}}_{33} \tag{14}$$

$$\alpha^{\mathrm{av}}_{33} = {}^1\!/_3(1 - F^{\mathrm{am}}_{200})(\alpha^{\mathrm{ao}}_{11} + \alpha^{\mathrm{ao}}_{22}) + {}^1\!/_3(2F^{\mathrm{am}}_{200} + 1)\alpha^{\mathrm{ao}}_{33} \tag{15}$$

where $\alpha^{\mathrm{co}}_{uv}$ and $\alpha^{\mathrm{ao}}_{uv}$ are the intrinsic linear thermal expansion coefficients of the crystalline and amorphous phases, respectively.

The problem that now arises is how the values of S^{co}_{uv} and S^{ao}_{uv} can be determined theoretically. Unfortunately, as discussed in a previous article,[2] there has been no report on this subject. Hence the theoretical values of S^{co}_{uv} were estimated from the inverse matrix of elastic stiffness C^{co}_{uv} proposed by Odajima and Maeda[5] because their value (253 GPa) of $1/S^{\mathrm{co}}_{33}$ fits our experimental value[6] better than other theoretical results.[7,8]

According to their report,[5] S^{co}_{uv} can be determined according to eq 16. The value in eq 16 is used in the case

$$|S^{\mathrm{co}}_{uv}| = \begin{vmatrix} S^{\mathrm{co}}_{11} & S^{\mathrm{co}}_{12} & S^{\mathrm{co}}_{13} & 0 & 0 & 0\\ S^{\mathrm{co}}_{12} & S^{\mathrm{co}}_{22} & S^{\mathrm{co}}_{23} & 0 & 0 & 0\\ S^{\mathrm{co}}_{13} & S^{\mathrm{co}}_{23} & S^{\mathrm{co}}_{33} & 0 & 0 & 0\\ 0 & 0 & 0 & S^{\mathrm{co}}_{44} & 0 & 0\\ 0 & 0 & 0 & 0 & S^{\mathrm{co}}_{55} & 0\\ 0 & 0 & 0 & 0 & 0 & S^{\mathrm{co}}_{66} \end{vmatrix} = \begin{vmatrix} 21.4 & -2.76 & -0.150 & 0 & 0 & 0\\ -2.76 & 12.0 & -0.246 & 0 & 0 & 0\\ -0.150 & -0.246 & 0.396 & 0 & 0 & 0\\ 0 & 0 & 0 & 3.53 & 0 & 0\\ 0 & 0 & 0 & 0 & 128.2 & 0\\ 0 & 0 & 0 & 0 & 0 & 48.5 \end{vmatrix} \times 10^{-2}/\mathrm{GPa} \tag{16}$$

of elevated temperature, since the crystal lattice modulus is independent of temperature, below the equilibrium melting point (145.5 °C) as shown in Figures 2 and 3 in ref 1.

The elastic compliance S^{ao}_{uv} of the amorphous phase is quite uncertain. However, it can be calculated from the potential energy of neighboring chains by assuming that the following relation between the potential energy $P(r)$ and the atomic or molecular distance r holds for an amorphous chain, although this treatment is a very crude approximation based on the hypothesis of a biphasic structure of crystalline and amorphous materials:[9]

$$P(r) = -c/r^n + d/r^m \tag{17}$$

where $m = 9$–12 and $n = 1$ or 6 for an ionic or molecular crystal, respectively. When the volume expansion of the amorphous phase is assumed to occur only along the lateral direction of the polymer chains, the elastic compliances S_{11}^{ao} and S_{22}^{ao} may be estimated by taking the second derivative of eq 17. They are given by

$$S_{11}^{ao} = S_{33}^{ao} = \{v_a(T)/v_c\}^4 S_{11}^{c'} \tag{18}$$

where $v_a(T)$ and v_c are, respectively, the volumes of the amorphous phase at an arbitrary temperature T and of the chain crystalline phase. In eq 18, $v_a(T)$ is an unknown parameter. If the linear thermal expansion of the amorphous phase is also assumed to occur only along the lateral direction, we have

$$v_a(T) = v_a\{1 + \alpha_a(T - T_0)\}\{1 + \alpha_b(T - T_0)\} \tag{19}$$

where v_a is the volume at T_0 and α_a and α_b are the thermal expansion coefficients of the crystal a and b axes, respectively. Then

$$S_{11}^{ao} = S_{22}^{ao} = (\rho_a/\rho_c)\{1 + \alpha_a(T - T_0)\}^4\{1 + \alpha_b(T - T_0)\}^4 S_{11}^{c'} \tag{20}$$

The values of α_a and α_b were obtained as 2.27×10^{-4} and 6.46×10^{-5} by plotting the dimensions of the crystal a and b axes against temperature, by using the date of Davis et al.[10]

The compliance S_{33}^{ao} may be estimated by assuming that the modulus along the chain axis is proportional to the number of chain molecules in the unit area perpendicular to the chain direction and that the modulus is independent of temperature. Thus, we have

$$S_{33}^{ao} = (\rho_c/\rho_a)S_{33}^{c'} \tag{21}$$

where ρ_a and ρ_c are the densities of the crystalline and amorphous phases, respectively. The compliances $S_{11}^{c'}$ and $S_{33}^{c'}$ in eq 18 and 21 correspond to S_{11}^{cv} and S_{33}^{cv} at $\theta = 0°$ (see eq A1 and A3 in Table II in the Appendix). That is

$$S_{11}^{c'} = {}^1\!/_8(3S_{11}^{co} + 3S_{22}^{co} + 2S_{12}^{co} + S_{66}^{co}) \tag{22}$$

$$S_{33}^{c'} = S_{33}^{co} \tag{23}$$

According to an estimate by Hibi et al.,[11] the other compliances can be represented as

$$S_{12}^{ao} = -\nu_{21}^{ao}S_{11}^{ao}$$

$$S_{13}^{ao} = -\nu_{31}^{ao}S_{33}^{ao}$$

$$S_{55}^{ao} = S_{44}^{ao} = 2(S_{11}^{ao} + \nu_{31}^{ao}S_{33}^{ao})$$

$$S_{66}^{ao} = 2S_{11}^{ao}(1 + \nu_{21}^{ao}) \tag{24}$$

The Poisson's ratios ν_{21}^{ao} and ν_{31}^{ao} are set to be 0.45 on the assumption that the mechanical properties of the amorphous phase are similar to those of a system showing ideal rubber elasticity but being somewhat tougher.

From the procedures discussed above, all the parameters except the orientation factors of the amorphous chain segments, F_{200}^{am} and F_{400}^{am}, can be determined.

By use of eq 8–11, the bulk strain ϵ_{33} can be separated into two components; one is ϵ_{33}^{σ}, associated with the external applied stress, and the other is ϵ_{33}^{T}, associated with the thermal expansion effect. That is

$$\epsilon_{33} = \epsilon_{33}^{\sigma} + \epsilon_{33}^{T} \tag{25}$$

where

$$\epsilon_{33}^{\sigma} = [x_c\{H_1(S_{uv}^{cv},S_{uv}^{av},X_c) + S_{33}^{cv}\} + (1 - X_c) \times \{G_1(S_{uv}^{cv},S_{uv}^{av},X_c) + S_{33}^{av}\}]\sigma_{33} \tag{26}$$

$$\epsilon_{33}^{T} = [X_c\{H_2(S_{uv}^{cv},S_{uv}^{av},X_c) + \alpha_{33}^{cv}\} + (1 - X_c) \times \{G_2(S_{uv}^{cv},S_{uv}^{av},X_c) + \alpha_{33}^{av}\}]\Delta T \tag{27}$$

where

$$H_1(S_{uv}^{cv},S_{uv}^{av},X_c) = 2S_{13}^{cv}(S_{13}^{av} - S_{13}^{cv})\Big/\left\{S_{12}^{cv} + S_{11}^{cv} + \frac{X_c}{1 - X_c}(S_{11}^{av} + S_{12}^{av})\right\} \tag{28}$$

$$G_1(S_{uv}^{cv},S_{uv}^{av},X_c) = 2X_cS_{13}^{av}(S_{13}^{cv} - S_{13}^{av})/(1 - X_c) \times \left\{S_{12}^{cv} + S_{11}^{cv} + \frac{X_c}{1 - X_c}(S_{11}^{av} - S_{12}^{av})\right\} \tag{29}$$

$$H_2(S_{uv}^{cv},S_{uv}^{av},X_c) = 2S_{11}^{cv}(\alpha_{11}^{av} - \alpha_{11}^{cv})\Big/\left\{S_{11}^{cv} + S_{12}^{cv} + \frac{X_c}{1 - X_c}(S_{11}^{av} + S_{12}^{av})\right\} \tag{30}$$

$$G_2(S_{uv}^{cv},S_{uv}^{av},X_c) = 2X_cS_{13}^{av}(\alpha_{11}^{cv} - \alpha_{11}^{av})/(1 - X_c) \times \left\{S_{11}^{cv} + S_{12} + \frac{X_c}{1 - X_c}(S_{11}^{av} + S_{12}^{av})\right\} \tag{31}$$

Thus, the Young's modulus E may be given by

$$E = \sigma_{33}/\epsilon_{33}^{\sigma} = 1/[x_c\{H_1(S_{uv}^{cv},S_{uv}^{av},X_c) + S_{33}^{cv}\} + (1 - X_c) \times \{G_1(S_{uv}^{cv},S_{uv}^{av},X_c) + S_{33}^{av}\}] \tag{32}$$

Returning to Figure 3, we should noted that the (002) plane can be detected by X-ray diffraction only when the crystal stain axes are oriented perfectly in the stretching direction. Accordingly, in the stress field σ_{uv}^{c} of the crystalline phase, the crystal lattice strain ϵ_{33}^{co} of the (002) plane detected by X-ray diffraction measurement can be represented as follows:

$$\epsilon_{33}^{co} = S_{13}^{co}\sigma_{11}^{c} + S_{23}^{co}\sigma_{22}^{c} + S_{33}^{co}\sigma_{33}^{c} + \alpha_{33}^{co}\Delta T \tag{33}$$

In eq 33, σ_{11}^{c} and σ_{22}^{c} can be represented as a function of σ_{33} (σ_{33}^{c}) by using eq 8–11. We then have

$$\epsilon_{33}^{co} = \{-F_1(S_{uv}^{co},S_{uv}^{cv},S_{uv}^{av},X_c) + S_{33}^{co}\}\sigma_{33} + \{-F_2(S_{uv}^{co},S_{uv}^{cv},S_{uv}^{av},X_c) + \alpha_{33}^{co}\}\Delta T \tag{34}$$

where

$$F_1(S_{uv}^{co},S_{uv}^{cv},S_{uv}^{av},X_c) = (S_{13}^{co} + S_{23}^{co})(S_{13}^{cv} - S_{13}^{av})\Big/\left\{S_{11}^{cv} + S_{12}^{cv} + \frac{X_c}{1 - X_c}(S_{11}^{av} + S_{12}^{av})\right\} \tag{35}$$

$$F_2(S_{uv}^{co},S_{uv}^{cv},S_{uv}^{av},X_c) = (\alpha_{11}^{cv} - \alpha_{11}^{av})(S_{13}^{co} + S_{23}^{co})\Big/\left\{S_{11}^{cv} + S_{12}^{cv} + \frac{X_c}{1 - X_c}(S_{11}^{av} + S_{12}^{av})\right\} \tag{36}$$

Here ϵ_{33}^{co} is given as two functions of stress and temperature. We then rewrite ϵ_{33}^{co} as $\epsilon_{33}^{co}(\sigma,T)$. When σ $(=\sigma_{33}) = 0$, eq 34 reduces to

$$\epsilon_{33}^{co}(0,T) = \{-F_2(S_{uv}^{co},S_{uv}^{cv},S_{uv}^{av},X_c) + \alpha_{33}^{co}\}\Delta T \tag{37}$$

We then have

$$\epsilon_{33}^{co}(\sigma,T) - \epsilon_{33}^{co}(0,T) = \{-F_1(S_{uv}^{co},S_{uv}^{cv},S_{uv}^{av},X_c) + S_{33}^{co}\}\sigma \tag{38}$$

X-ray diffraction measurements have the advantages of distinguishing between $\epsilon_{33}^{co}(\sigma,T)$ and $\epsilon_{33}^{co}(0,T)$. The crystal strain in the absence of applied external stress corresponds to $\epsilon_{33}^{co}(0,T)$. Since ϵ_{33}^{co} in eq 34 can be represented as $\epsilon_{33}^{co}(\sigma,T)$, the following relation can be constructed:

$$S_{33}^{c} = \frac{\epsilon_{33}(\sigma,T) - \epsilon_{33}^{co}(0,T)}{\sigma} = -F_1(S_{uv}^{co},S_{uv}^{cv},S_{uv}^{av},X_c) + S_{33}^{co} \tag{39}$$

$$E_c = 1/S_{33}^{c} = 1/\{-F_1(S_{uv}^{co},S_{uv}^{cv},S_{uv}^{av},X_c) + S_{33}^{co}\} \tag{40}$$

where E_c corresponds to the crystal lattice modulus of the crystal (002) plane detected by X-ray diffraction. Here

Table I
Orientation Factors, F_{200}^{am} and F_{400}^{am}, of Cases I and II[a]

orientation mode of amorphous chain segments	λ	orientation factors	
		F_{200}^{am}	F_{400}^{am}
case I		0.999 99	0.999 98
case II	50	0.993 36	0.987 58
	100	0.997 65	0.995 59
	200	0.999 17	0.998 44

[a] In case II, the factors were calculated from eq 42.

the measured value E_c is essentially different from the intrinsic crystal lattice modulus E_c^o $(=1/S_{33}^{co})$ in the molecular chain direction. When $F_1(S_{uv}^{co},S_{uv}^{cv},S_{uv}^{av},X_c) \ll S_{33}^{co}$, E_c is almost equal to E_c^o. Calculations to check the significance of the above relation are given later.

Furthermore, from eq 34, we have

$$\alpha_{33}^{c} = \frac{\epsilon_{33}(\sigma,T) - \epsilon_{33}^{co}(\sigma,T_0)}{\Delta T} = -F_2(S_{uv}^{co},S_{uv}^{cv},S_{uv}^{av},X_c) + \alpha_{33}^{co} \tag{41}$$

where α_{33}^{c} corresponds to the linear thermal expansion coefficient of the crystal (002) plane detected by X-ray diffraction. Equation 41 indicates that α_{33}^{c} is quite different from α_{33}^{co}, which denotes the intrinsic thermal expansion coefficient of the crystal c axis. When $F_2(S_{uv},S_{uv},S_{uv},X_c) \ll \alpha_{33}^{co}$, α_{33}^{c} is almost equal to α_{33}^{co}. Unfortunately, there is no information on the thermal expansion behavior of the crystalline and amorphous phases represented by eq 12–15. However, if $\alpha_{11}^{cv} = \alpha_{11}^{av}$, $F_2(S_{uv}^{co},S_{uv}^{cv},S_{uv}^{av},X_c)$ becomes zero and α_{33}^{c} is equivalent to α_{33}^{co}.

Discussion

Evaluation of the orientation of amorphous chain segments is indispensable for carrying out numerical calculations. As discussed in ref 1, however, it is difficult to estimate the orientation factors, F_{200}^{am} and F_{400}^{am}, from birefringence. Accordingly, the orientation factors are calculated on the basis of the following assumptions: the orientation of the amorphous chain segments is equal to that of the c axes (case I) or it behaves in an affine fashion (case II), which is given by

$$\omega(\cos\theta) = \frac{\lambda^3}{\{\lambda^3 - (\lambda^3 - 1)\cos^2\theta\}^{3/2}} \tag{42}$$

where λ is the draw ratio of amorphous chain segments from a random state.

It is unfortunate to assume the orientation of amorphous chain segments in an affine fashion. Actually, recent neutron-scattering studies indicate that the radius of affine gyration of the polyethylene chain deviates from the affine fashion even at an elongation ratio <5.[12]

Table I lists the orientation factors F_{200}^{am} and F_{400}^{am} for cases I and II. The factors increase as λ increases, but the degree of orientation is much lower than the crystal orientation. The numerical calculation was carried out by using these values in Table I.

Figure 4 shows the change in E/E_c (the Young's modulus/the crystal lattice modulus) with temperature. The crystallinity is fixed at 97%, which corresponds to the experimental result at room temperature. The curves are calculated for various values of λ, the draw ratio of amorphous chain segments. The orientation factors, F_{200} and F_{400}, of crystallites used in the calculation were 0.999 99 and 0.999 98, respectively, from the X-ray diffraction measurements. The value of E/E_c is almost independent of temperature, and this tendency becomes somewhat more marked as λ increases. Finally, the value of E/E_c becomes close to unity when the amorphous chain segments are oriented perfectly with respect to the stretching direction as in case I.

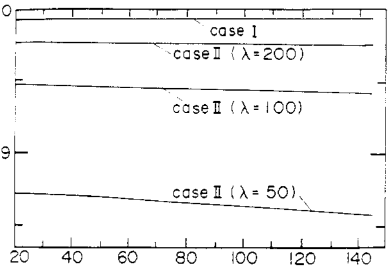

Figure 4. Theoretical results of temperature dependence of E/E_c with various draw ratios of amorphous chain segments, in which crystallinity was set to be 97%.

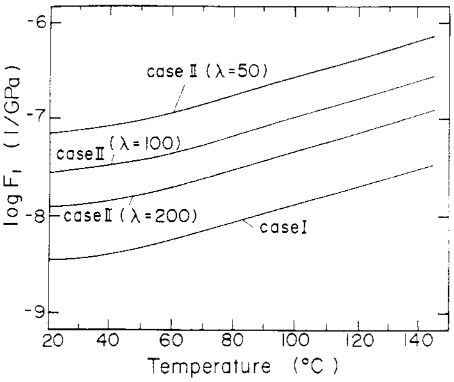

Figure 5. Logarithmic value of F_1 calculated as a function of temperature for various draw ratios of amorphous chain segments.

Figure 5 shows the change in log F_1 with temperature. This calculation was carried out by using the crystallinites as a function of temperature in Figure 7 in ref 1. The values of F_1 calculated in cases I and II are much lower than S_{33}^{co} $(0.396 \times 10^{-2}/\mathrm{GPa})$. This indicates that from eq 39 and 40 S_{33}^{c} is almost equal to S_{33}^{co}, and thus E_c is almost equal to E_c^o. This means that the crystal lattice modulus of the crystal (002) plane detected by X-ray diffraction is almost equal to the intrinsic crystal modulus in the chain direction.

As discussed in ref 1, the temperature dependence of crystallinity was estimated from the decrease in the X-ray intensity distribution curve from the (002) plane with increasing temperature. In this process, the thermal fluctuation of atoms within crystallites reported by Ruland[13,14] and Kilian[15,16] was neglected because of the difficulty of the measurement. Namely, the specimen was torn at the position where it was irradiated by the X-ray beam for 3 h at temperature above 80 °C, since the sample thickness was less than 4 μm. This omission, however, is thought to be reasonable for the ultradrawn specimen because of the experimental result that the crystal lattice modulus is independent of temperature up to 145 °C.[1] The preparation of ultradrawn films thick enough to estimate the thermal fluctuation by X-ray diffraction is needed to check our assumption.

Figure 6 shows the change in E_c with temperature. The value is almost independent of the orientation degree of amorphous chain segments for the specimens with draw ratios >50. The value of E_c is almost equal to the theoretical E_c^o given by Odajima and Maeda.[5] This result supports those in Figure 5, which are in good agreement with the experimental results in Figures 2 and 3 in ref 1.

Figure 7 shows the theoretical and experimental values of E/E_c as a function of temperature. The theoretical

Table II
Elastic Compliance S_{uv} Formulated by S^{co}_{uv} Using Eq 2-7

$$\begin{aligned}S_{11} = {} & (1/64)S^{\circ}_{11}\{(1/2520)F_{444} - (1/315)F_{442} + (1/35)F_{440} - (1/315)F_{424} + (8/315)F_{422} - (8/35)F_{420} + (1/35)F_{404} - (8/35)F_{402} + \\ & (72/35)F_{400} + (16/7)F_{222} - (32/7)F_{200} - (32/7)F_{202} + (64/7)F_{200} + 64/5\} + (1/64)S^{\circ}_{22}\{(1/2520)F_{444} + (1/315)F_{442} + (1/35)F_{440} - \\ & (1/315)F_{424} - (8/315)F_{422} - (8/35)F_{420} + (1/35)F_{404} + (8/35)F_{402} + (72/35)F_{400} - (16/7)F_{222} - (32/7)F_{220} + (32/7)F_{202} + \\ & (64/7)F_{200} + 64/5\} + (1/56)S^{\circ}_{33}\{(1/15)F_{440} - (8/15)F_{420} + (24/5)F_{400} + 8F_{220} - 16F_{200} + 56/5\} + (1/64)(2S^{\circ}_{12} + S^{\circ}_{66})\{-(1/2520)F_{444} + \\ & (1/105)F_{440} + (1/315)F_{424} - (8/105)F_{420} - (1/35)F_{404} + (24/35)F_{400} - (32/21)F_{220} + (64/21)F_{200} + 64/15\} + (1/112)(2S^{\circ}_{13} + \\ & S^{\circ}_{55})\{(1/180)F_{442} - (1/15)F_{440} - (2/45)F_{422} + (8/15)F_{420} + (2/5)F_{402} - (24/5)F_{400} + (2/3)F_{222} + (4/3)F_{220} - (4/3)F_{202} - (8/3)F_{200} + \\ & 112/15\} + (1/112)(2S^{\circ}_{23} + S^{\circ}_{44})\{-(1/180)F_{442} - (1/15)F_{440} + (2/45)F_{422} + (8/15)F_{420} - (2/5)F_{402} - (24/5)F_{400} - \\ & (2/3)F_{222} + (4/3)F_{220} + (4/3)F_{202} - (8/3)F_{200} + 112/15\}\end{aligned} \tag{A1}$$

$$\begin{aligned}S_{22} = {} & (1/64)S^{\circ}_{11}\{(1/2520)F_{444} - (1/315)F_{442} + (1/35)F_{440} + (1/315)F_{424} - (8/315)F_{442} + (8/35)F_{420} + (1/35)F_{404} - (8/35)F_{402} + \\ & (72/35)F_{400} - (16/7)F_{222} + (32/7)F_{220} - (32/7)F_{202} + (64/7)F_{200} + 64/5\} + (1/64)S^{\circ}_{22}\{(1/2520)F_{444} + (1/315)F_{442} + (1/35)F_{440} + \\ & (1/315)F_{424} + (8/315)F_{422} + (8/35)F_{420} + (1/35)F_{404} + (8/35)F_{402} + (72/35)F_{400} + (16/7)F_{222} + (32/7)F_{220} + (32/7)F_{202} + \\ & (64/7)F_{200} + 64/5\} + (1/56)S^{\circ}_{33}\{(1/15)F_{440} + (8/15)F_{420} + (24/7)F_{400} - 8F_{220} - 16F_{200} + 56/5\} + (1/64)(2S^{\circ}_{12} + S^{\circ}_{66})\{-(1/2520)F_{444} + \\ & (1/105)F_{440} - (1/315)F_{424} + (8/105)F_{420} - (1/35)F_{404} + (24/35)F_{400} + (32/21)F_{220} + (64/21)F_{200} + 64/15\} + \\ & (1/112)(2S^{\circ}_{13} + S^{\circ}_{55})\{(1/180)F_{442} - (1/15)F_{440} + (2/45)F_{422} - (8/15)F_{420} + (2/5)F_{402} - (24/5)F_{400} - (2/3)F_{222} - (4/3)F_{220} - (4/3)F_{202} - \\ & (8/3)F_{200} + 112/15\} + (1/112)(2S^{\circ}_{23} + S^{\circ}_{44})\{-(1/180)F_{442} - (1/15)F_{440} - (2/45)F_{422} - (8/15)F_{420} - (2/5)F_{402} - (24/5)F_{400} - \\ & (2/3)F_{222} - (4/3)F_{220} + (4/3)F_{202} - (8/3)F_{200} + 112/15\}\end{aligned} \tag{A2}$$

$$\begin{aligned}S_{33} = {} & (1/56)S^{\circ}_{11}\{(1/15)F_{404} - (8/15)F_{402} + (24/5)F_{400} + 8F_{202} - 16F_{200} + 56/5\} + (1/56)S^{\circ}_{22}\{(1/15)F_{404} + (8/15)F_{402} + (24/5)F_{400} - \\ & 8F_{202} - 16F_{200} + 56/5\} + S^{\circ}_{33}\{(8/35)F_{400} + (4/7)F_{200} + 1/5\} + (1/56)(2S^{\circ}_{12} + S^{\circ}_{66})\{-(1/15)F_{404} + (8/5)F_{400} - (16/3)F_{200} + 56/15\} + \\ & (1/2)(2S^{\circ}_{13} + S^{\circ}_{55})\{(2/105)F_{402} - (8/35)F_{400} + (1/21)F_{202} + (2/21)F_{200} + 2/15\} + (1/2)(2S^{\circ}_{23} + S^{\circ}_{44})\{-(2/105)F_{402} - (8/35)F_{400} - \\ & (1/21)F_{202} + (2/21)F_{200} + 2/15\}\end{aligned} \tag{A3}$$

$$\begin{aligned}S_{12} = {} & (1/64)S^{\circ}_{11}\{-(1/2520)F_{444} + (1/315)F_{442} - (1/35)F_{440} + (1/105)F_{404} - (8/105)F_{402} + (24/35)F_{400} - (32/21)F_{202} + (64/21)F_{200} + \\ & 64/15\} + (1/64)S^{\circ}_{22}\{-(1/2520)F_{444} - (1/315)F_{442} - (1/35)F_{440} + (1/105)F_{404} + (8/105)F_{402} + (24/35)F_{400} + (32/21)F_{202} + \\ & (64/21)F_{200} + 64/15\} + (1/8)S^{\circ}_{33}\{-(1/105)F_{440} + (8/35)F_{400} - (16/21)F_{200} + 56/105\} + S^{\circ}_{12}\{(1/80640)F_{444} - (1/3360)F_{440} - \\ & (1/3360)F_{404} + (1/140)F_{400} + (10/21)F_{200} + 4/15\} + (1/7)S^{\circ}_{13}\{(1/1440)F_{442} + (1/120)F_{440} + (1/60)F_{402} - (1/5)F_{400} - (5/6)F_{202} - \\ & (5/3)F_{200} + 28/15\} + (1/7)S^{\circ}_{23}\{-(1/1440)F_{442} + (1/120)F_{440} - (1/60)F_{402} - (1/5)F_{400} + (5/6)F_{202} - (5/3)F_{200} + 28/15\}\end{aligned} \tag{A4}$$

$$\begin{aligned}S_{13} = {} & (1/112)S^{\circ}_{11}\{(1/180)F_{424} - (2/45)F_{422} + (2/5)F_{420} - (1/15)F_{404} + (8/15)F_{402} - (24/5)F_{400} + (2/3)F_{222} - (4/3)F_{220} + (4/3)F_{202} - \\ & (8/3)F_{200} + 112/15\} + (1/112)S^{\circ}_{22}\{(1/180)F_{424} + (2/45)F_{422} + (2/5)F_{420} - (1/15)F_{404} - (8/15)F_{402} - (24/5)F_{400} - (2/3)F_{222} - \\ & (4/3)F_{220} - (4/3)F_{202} - (8/3)F_{200} + 112/15\} + S^{\circ}_{33}\{(1/105)F_{420} - (4/35)F_{400} + (1/42)F_{220} + (1/21)F_{200} + 1/15\} + \\ & (1/7)S^{\circ}_{12}\{-(1/1440)F_{424} + (1/60)F_{420} + (1/120)F_{404} - (1/5)F_{400} - (5/6)F_{220} - (5/3)F_{200} + 28/15\} + S^{\circ}_{13}\{(1/1260)F_{422} - \\ & (1/105)F_{420} - (1/105)F_{420} - (1/105)F_{402} + (4/35)F_{400} + (5/168)F_{222} - (1/12)F_{202} + (5/42)F_{200} + 28/105\} + S^{\circ}_{23}\{-(1/1260)F_{422} + \\ & (1/105)F_{402} + (4/35)F_{400} - (5/168)F_{222} + (1/12)F_{220} - (5/84)F_{202} + (5/42)F_{200} + 28/105\}\end{aligned} \tag{A5}$$

$$\begin{aligned}S_{23} = {} & (1/112)S^{\circ}_{11}\{-(1/180)F_{424} + (2/45)F_{422} - (2/7)F_{420} - (1/15)F_{404} + (8/15)F_{402} - (24/5)F_{400} - (2/3)F_{222} + (4/3)F_{220} + (4/3)F_{202} - \\ & (8/3)F_{200} + 112/15\} + (1/112)S^{\circ}_{22}\{-(1/180)F_{424} - (2/45)F_{422} - (2/5)F_{420} - (1/15)F_{404} - (8/15)F_{402} - (24/5)F_{400} + (2/3)F_{222} + \\ & (4/3)F_{220} - (4/3)F_{202} - (8/3)F_{200} + 112/15\} + S^{\circ}_{33}\{-(1/105)F_{420} - (4/35)F_{400} + (1/42)F_{220} + (1/21)F_{200} + 1/15\} + \\ & (1/7)S^{\circ}_{12}\{(1/1440)F_{424} - (1/60)F_{420} + (1/120)F_{404} - (1/5)F_{400} + (5/6)F_{220} - (5/3)F_{200} + 28/15\} + (1/7)S^{\circ}_{13}\{-(1/180)F_{422} + \\ & (1/15)F_{420} - (1/15)F_{402} + (4/5)F_{400} - (5/24)F_{222} - (5/12)F_{220} - (5/12)F_{202} + (5/6)F_{200} + 28/15\} + \\ & (1/7)S^{\circ}_{23}\{(1/180)F_{422} + (1/30)F_{420} + (1/15)F_{402} + (4/5)F_{400} + (5/24)F_{222} + (1/12)F_{220} - (5/12)F_{202} + (5/6)F_{200} + 28/15\}\end{aligned} \tag{A6}$$

$$\begin{aligned}S_{44} = {} & (1/112)S^{\circ}_{11}\{-(1/180)F_{424} + (2/45)F_{422} - (2/5)F_{420} - (1/15)F_{404} + (8/15)F_{402} - (24/5)F_{400} - (2/3)F_{222} + (4/3)F_{220} + (4/3)F_{202} - \\ & (8/3)F_{200} + 112/15\} + (1/112)S^{\circ}_{22}\{-(1/180)F_{424} - (2/45)F_{422} - (6/15)F_{420} - (1/15)F_{404} - (8/15)F_{402} - (24/5)F_{400} + (2/3)F_{222} + \\ & (4/3)F_{220} - (4/3)F_{202} - (8/3)F_{200} + 112/15\} + S^{\circ}_{33}\{-(1/105)F_{420} - (4/35)F_{400} + (1/42)F_{220} + (1/21)F_{200} + 1/15\} + \\ & (1/4)S^{\circ}_{66}\{(1/10080)F_{424} - (1/420)F_{420} + (1/840)F_{404} - (1/35)F_{400} + (5/42)F_{220} - (5/21)F_{200} + 4/15\} + (1/28)S^{\circ}_{55}\{-(1/180)F_{442} + \\ & (1/15)F_{420} - (1/15)F_{402} + (4/5)F_{400} - (5/24)F_{222} - (5/12)F_{220} + (5/12)F_{202} + (5/6)F_{200} + 28/15\} + \\ & (1/28)S^{\circ}_{44}\{(1/180)F_{422} + (1/30)F_{420} + (1/15)F_{402} + (4/5)F_{400} + (5/24)F_{222} + (1/12)F_{220} - (5/12)F_{202} + (5/6)F_{200} + 28/15\}\end{aligned} \tag{A7}$$

$$\begin{aligned}S_{55} = {} & (1/112)S^{\circ}_{11}\{(1/180)F_{424} - (2/45)F_{422} + (2/35)F_{420} - (1/15)F_{404} + (8/15)F_{402} - (24/5)F_{400} + (2/3)F_{222} - (4/3)F_{220} + (4/3)F_{202} - \\ & (8/3)F_{200} + 112/15\} + (1/112)S^{\circ}_{22}\{(1/180)F_{424} + (2/45)F_{422} + (2/5)F_{420} - (1/15)F_{404} - (8/15)F_{402} - (24/5)F_{400} - (2/3)F_{222} - \\ & (4/3)F_{220} - (4/3)F_{202} - (8/3)F_{200} + 112/15\} + S^{\circ}_{33}\{(1/105)F_{420} - (4/35)F_{400} + (1/42)F_{220} + (1/21)F_{200} + 1/15\} + \\ & (1/28)S^{\circ}_{66}\{-(1/1440)F_{424} + (1/60)F_{420} + (1/120)F_{404} - (1/5)F_{400} - (5/6)F_{220} - (5/3)F_{200} + 28/15\} + (1/28)S^{\circ}_{55}\{(1/180)F_{422} - \\ & (1/15)F_{420} - (1/15)F_{402} + (4/5)F_{400} + (5/24)F \\ & (1/15)F_{420} - (1/15)F_{402} + (4/5)F_{400} + (5/24)F_{222} + (5/12)F_{220} + (5/12)F_{202} + (5/6)F_{200} + 28/15\} + \\ & (1/28)S^{\circ}_{44}\{-(1/180)F_{422} + (1/15)F_{402} + (4/5)F_{400} - (5/24)F_{222} + (5/12)F_{220} - (5/12)F_{202} + (5/6)F_{200} + 28/15\}\end{aligned} \tag{A8}$$

$$\begin{aligned}S_{66} = {} & (1/64)S^{\circ}_{11}\{-(1/2520)F_{444} + (1/315)F_{442} - (1/35)F_{440} + (1/105)F_{404} - (8/105)F_{402} + (24/35)F_{400} - (32/21)F_{202} + (64/21)F_{200} + \\ & 64/15\} + (1/64)S^{\circ}_{22}\{-(1/2520)F_{444} - (1/315)F_{442} - (1/35)F_{440} + (1/105)F_{404} + (8/105)F_{402} + (24/35)F_{400} + (32/21)F_{202} + \\ & (64/21)F_{202} + 64/15\} + (1/56)S^{\circ}_{33}\{-(1/15)F_{440} + (8/5)F_{400} - (16/3)F_{200} + 56/15\} + (1/28)S^{\circ}_{66}\{(1/11520)F_{444} - (1/480)F_{440} - \\ & (1/480)F_{404} + (1/20)F_{400} + (10/3)F_{200} + 28/15\} + (1/28)S^{\circ}_{55}\{-(1/1440)F_{442} + (1/120)F_{440} + (1/60)F_{402} - (1/5)F_{400} - (5/6)F_{202} - \\ & (5/3)F_{200} + 28/15\} + (1/28)S^{\circ}_{44}\{(1/1440)F_{442} + (1/120)F_{440} - (1/60)F_{402} - (1/5)F_{400} + (5/6)F_{202} - (5/3)F_{200} + 28/15\}\end{aligned} \tag{A9}$$

where

$$F_{200} = (1/2)(3\langle\cos^2\theta\rangle - 1) \tag{A10}$$

$$F_{202} = 3\langle\sin^2\theta\cos 2\eta\rangle \tag{A11}$$

$$F_{220} = 3\langle\sin^2\theta\cos 2\phi\rangle \tag{A12}$$

$$F_{222} = \langle(1/4)(1 + \cos\theta)^2\cos 2\phi\cos 2\eta\rangle \tag{A13}$$

$$F_{400} = (1/8)\{35\langle\cos^4\theta\rangle - 30\langle\cos^2\theta\rangle + 3\} \tag{A14}$$

$$F_{402} = (15/2)\langle(7\cos^2\theta - 1)\sin^2\theta\cos 2\eta\rangle \tag{A15}$$

$$F_{404} = 105\langle\sin^4\theta\cos 4\eta\rangle \tag{A16}$$

$$F_{420} = (15/2)\langle(7\cos^2\theta - 1)\sin^2\theta\cos 2\phi\rangle \tag{A17}$$

$$F_{440} = 105\langle\sin^4\theta\cos 4\phi\rangle \tag{A18}$$

$$F_{422} = 90\langle(7\cos^4\theta - 6\cos^2\theta + 1)\cos 2\phi\cos 2\eta\rangle \tag{A19}$$

$$F_{424} = 1260\langle(\cos^4\theta - 1)\cos 2\phi\cos 4\eta\rangle \tag{A20}$$

$$F_{422} = 1260\langle(\cos^4\theta - 1)\cos 4\phi\cos 2\eta\rangle \tag{A21}$$

$$F_{444} = 2520\langle(\cos^4\theta + 6\cos^2\theta + 1)\cos 4\phi\cos 4\eta\rangle \tag{A22}$$

values were calculated by using the crystallinities at the indicated temperature in Figure 7 in ref 1. In this calculation, however, the temperature dependence of the orientation of the amorphous chain segments is neglected

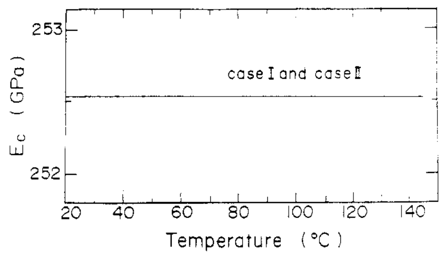

Figure 6. Crystal lattice modulus E_c calculated as a function of temperature for various draw ratios of amorphous chain segments.

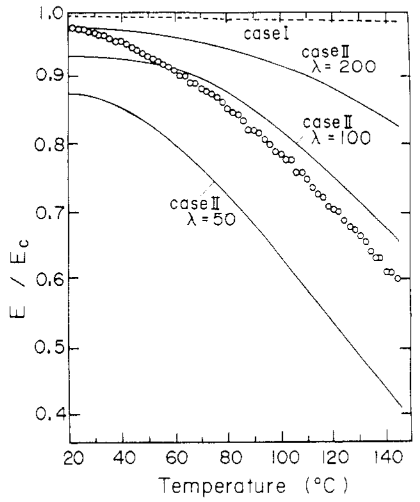

Figure 7. Theoretical and experimental results of E/E_c as a function of temperature for various draw ratios of amorphous chain segments. The experimental data are the same as in Figure 8 of ref 1.

because of the ambiguity of the birefringence data in Figure 11 in ref 1. The experimental result is in good agreement with the result calculated by substituting λ = 100 into eq 42, but a discrepancy remains because of neglecting the temperature dependence of the mobility of the polymer chains. It seems reasonable that the increasing mobility of polymer chains with increasing temperature causes a significant transition from crystalline to amorphous phases. However, the temperature dependence of the orientation of the amorphous chain segments cannot be determined from birefringence data, as discussed in ref 1. A mathematical representation must be proposed to give the best fit between experimental and theoretical results.

Conclusion

The temperature dependence of the crystal lattice modulus and the Young's modulus were formulated by a linear elastic theory based on the experimental results in the preceding article.[1] A composite structural unit was proposed as a model to calculate the mechanical anisotropy of a two-phase system on the basis of the homogeneous stress hypothesis by considering a structural unit composed of crystalline and amorphous phases. The theoretical elastic compliance of the crystal unit was estimated from the inverse matrix of elastic stiffness proposed by Odajima et al.,[5] while the elastic compliance of the amorphous phase was calculated from the relation between the Lennard-Jones potential function and the molecular distance. The calculated results suggest why the crystal lattice modulus is hardly affected by temperature while the Young's modulus is very sensitive.

Appendix

The elastic compliance S_{uv} can be formulated by S_{uv}^{co} from use of eq 2–7 as shown in Table II.

Equations A1–A9 represent the generalized formulation to estimate the relationship between the elastic compliance of the bulk specimen and that of the orthogonal unit.

When the structural unit has uniaxial orientation distribution around the x_3 axis as in the present system, S_{uv}^{cv} can be written simpler than eq A1–A9. For example, S_{11}^{cv}, S_{33}^{cv}, S_{12}^{cv}, and S_{13}^{cv} were represented in a previous paper.[2] Furthermore, the amorphous chain segments have uniaxial symmetry around the u_3 axis. Then the compliance S_{uv}^{av} can be written as simpler forms than S_{uv}^{cv}, and they were given as eq 15–18 in a previous paper.[2]

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